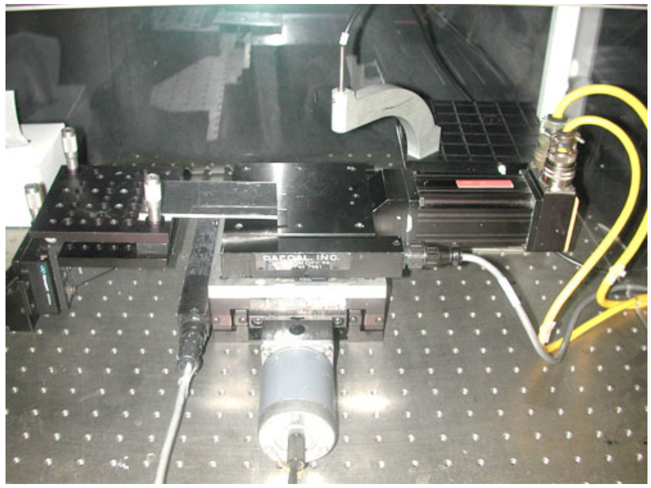

Thin Film Flow Coating

Specifications and Operation Guidelines

For gradients in
Film Thickness

MEASUREMENT • ANALYSIS • INFORMATICS • DESIGN • FABRICATION •

NIST **Combinatorial Methods Center**

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This document is intended as a basic guide for constructing an instrument but does not imply any agreement for continuing technical support. For more information, contact the NIST Combinatorial Methods Center at NCMChelp@nist.gov

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Last Update: October 2002 (Stafford)

1. Purpose and structure of this document

This document is provided by the NIST Combinatorial Methods Center as a guide for constructing and operating an instrument for creating thickness gradients of polymer thin films. First, the basic principles of this instrument will be described. Next, the components of the instrument and schemes for its construction are supplied. Here, the discussion is based upon the specific components and design of the NCMC device (see disclaimer, page 1). Next, guidelines for operating the instrument and some basic applications are outlined, including notes on computer control/automation and calibration.

2. Principles of the Thin Film Flow Coater.

Flow coating draws upon a competition between (1) capillary forces holding a volume of polymer solution between a stationary knife blade and a substrate, and (2) frictional drag exerted on that volume of solution as the blade is pulled across the substrate. At zero velocity, capillary forces will hold the volume of solution under the blade with a slight decrease in overall volume due to evaporation of solvent from edges. At low velocities, capillary forces aim to keep the material between the substrate and the blade, but the frictional drag causes a small amount of solution to escape from under the knife blade. This material is left in the form of a film, and the film dries by evaporation of solvent. At higher velocities, the frictional drag becomes greater and thus forces more solution to be left behind on the substrate in the form of a film. Ultimately, it is the instantaneous velocity that controls the thickness of the polymer solution left behind.

In this document, we will focus on two cases that can be used to prepare polymer thin films via flow coating. Case I would be applied when a uniform film thickness is desired (see Figure 2). In this case, the acceleration would be set as high as possible so that the stage quickly reaches the desired final velocity (v_f), and the stage will remain in motion at that velocity over the desired distance/length (D_f) of the film. The stage inevitably will need some distance to decelerate, but that can be set as high as possible as well. The result would be a uniform film with a thickness dictated by the final velocity

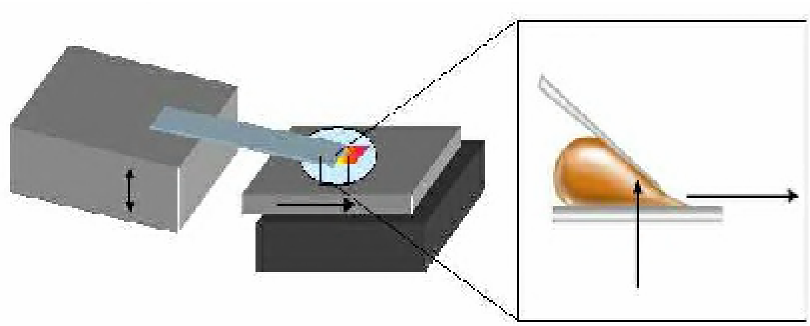

Figure 1. Schematic of the flow coating technique developed at NIST for preparing this polymer films. The thickness of the resulting film depends on the instantaneous velocity of the blade as it moves across the substrate.

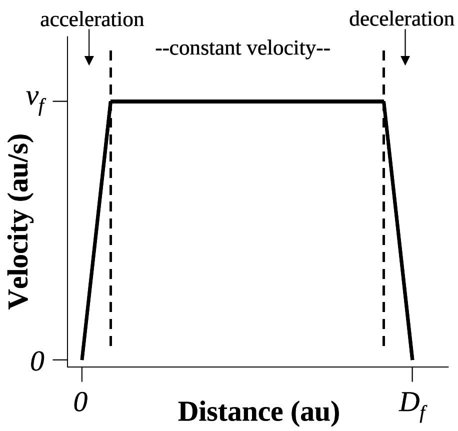

Figure 2.
Case I. Uniform film thickness:
Final velocity controls film thickness.

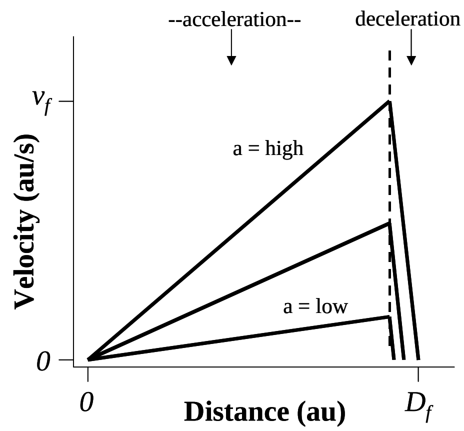

Figure 3.
Case II. Thickness gradient:
Acceleration controls film thickness

and with a length controlled by the total distance the stage travels. Case II would be applied when a gradient in film thickness is preferred (see Figure 3). In this case, the acceleration (more specifically, the instantaneous velocity at any given point in time) will control the resulting thickness range of the film. Here, the final velocity (ν_f) would be set as high as possible so that at the given acceleration, the final velocity will never be reached over the distance/length (D_f) of the film, as that would result in a plateau in the film thickness (see Case I). The result of this case would be a film with a gradient in film thickness, where the acceleration and total distance traveled would dictate the steepness of the gradient.

As this method relies on capillarity, frictional drag, and solvent evaporation, certain solution properties will dictate the thickness and uniformity of the resulting film. The viscosity and surface tension of the solution are arguably the most important parameters and will be a function of the polymer (MW, chain architecture, solvent interactions, etc) and the solvent. The volatility of the solvent is another important parameter, in that a solvent that evaporates too quickly (*i.e.* chloroform) will not allow the solution to flow and level while a solvent that evaporates too slowly (*i.e.* water) may cause the thickness gradient to be lost due to long range flow and leveling.

3. Design of the Thin Film Flow Coater

Figures 4 and 5 illustrate the Thin Film Flow Coater in plan view and side view as implemented by the NIST M3 Group. Individual device components are labeled (A-E) and described below.

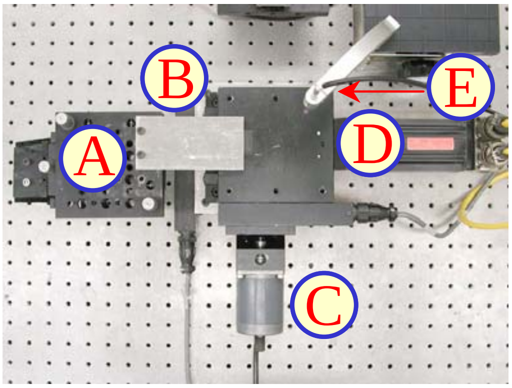

Figure 4. Plan view.

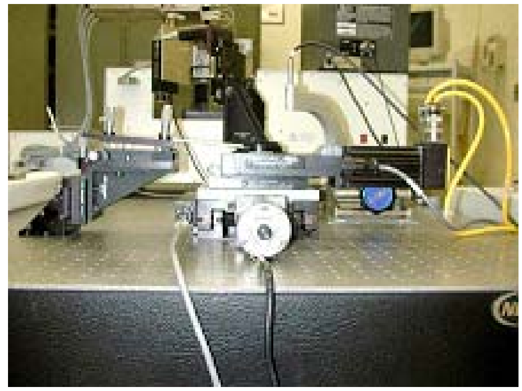

Figure 5. Side view.

- **A) Tip/Tilt/Height.** 3-axis tilt and rotation platform in tandem with height adjustment for knife blade alignment (Newport Models 37 and 460A, respectively, combined with Newport Model 360-90 right-angle brackets).
- **B) Knife Blade.** Glass slide attached to an aluminum plate.
- **C) Y-Axis Motor.** Computer-controlled 4" translation stage (Daedal Positioning, now part of Parker Automation).
- **D) X-Axis Motor.** Computer-controlled 2" translation stage (Parker Automation).
- **E) Interferometer.** Spot-interferometer for measurement of film thickness as a function of x-y position (Filmetrics F20).

NOTES:

- These specifications have been optimized for films having lateral dimensions of <50 mm and thicknesses <1 μm. We are currently designing and implementing a new flow coater that allows dimensions of 150 mm to be attained, as well as opening avenues to thick films and coatings.
- The simplest flow coater requires only one axis of motion (X-axis) to controllably move the substrate from underneath the knife blade. In the case presented here, the second axis (Y-axis) is utilized only for mapping the thickness of the film as a function of x-y position via interferometry.
- We initially used a simple putty knife as the knife blade and had great success. Refinement led to the use of a cleaved silicon wafer attached to an aluminum plate via epoxy to obtain a higher degree of smoothness than machined steel, but the epoxy layer led to bowing of the silicon blade. Further refinement has led

NOTES (cont')

to the use of a glass slide simply taped to the aluminum plate, allowing the blade to be both disposable and interchangeable. Blade widths can be 25 mm, 50 mm, or 75 mm (25x75 mm^2 or 50x75 mm^2 glass slides). The glass slide also allows for the bead of solution to be visible to the user during the loading of the solution underneath the blade as well as during deposition of the film.
- Other parameters that can control the film thickness: (1) volume of solution placed under the blade, and (2) height of the blade above the substrate. Observations have shown that volume of solution can have a minor yet noticeable effect on the resulting film thickness. To eliminate this variability, we hold the volume constant (per unit length of the blade). The blade height has been explored in detail in developing this technique, and the height (200 μm) was optimized for our applications of studying thin films.

4. Thin Film Flow Coater Use Guidelines.

Sample Preparation. Solutions should be filtered prior to using the flow coater. This eliminates any dust or other particulates from marring the final film and gives more uniform coatings. Substrates can be polished silicon wafers or glass slides, depending on the acceptable surface roughness of the substrate. Silicon wafers have one clear advantage in that thin polymer films show distinct interference colors upon reflection of light that are indicators of film thickness, therefore a quick visual inspection can ascertain if the sample is in the anticipated thickness range and free of defects. Appropriate measures should be taken to ensure the substrate is clean of adsorbed organic contaminants. Solvent rinsing followed by UV-ozone treatment for 20 minutes is usually sufficient, but certain applications may warrant 'piranha' etching, plasma cleaning, Nochromix, or HF treatment.

Sample Mounting. The surface of the translation stage should be clean and free of any large defects (residual film from a previous experiment, tape remnants, etc.) Defects will ultimately cause the substrate to be misaligned. The substrate is affixed to the translation stage by tape. Proper placement of the tape should be on opposite sides of the substrate to eliminate the potential for the substrate to 'lift up' before or during the coating process. The tape should also be carefully placed as to not interfere with the knife blade as it is moving across the substrate.

Knife Blade Alignment. The knife blade (glass slide) should be clean and free of defects. Rinsing with solvent and drying with compressed air or nitrogen is sufficient. If material on the blade cannot be removed using these steps, simply replace the glass slide with a new one from the box. The glass slide is secured to the aluminum plate via tape and the plate screwed into the tip/tilt/height fixture. At this point the substrate should also be affixed to the translation stage. The next step is to manually adjust the tip/tilt of the blade to ensure that it is parallel to the substrate surface. First, (1) lower the blade via the micrometer on the z-axis stage (height adjustment) until it barely

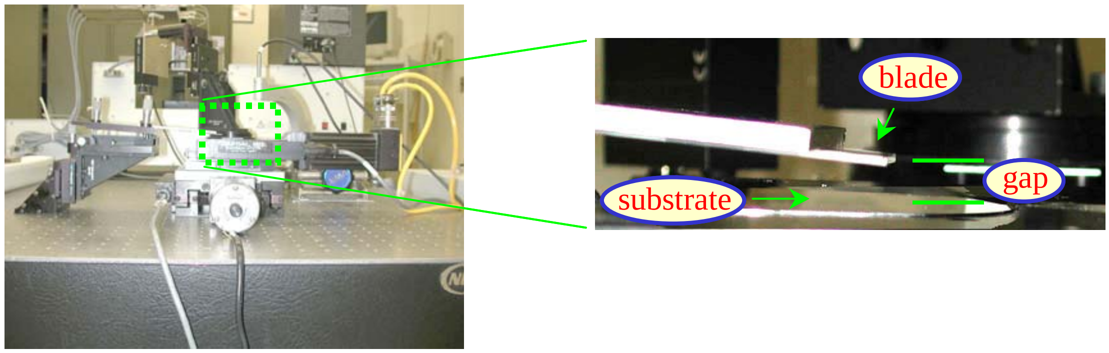

Figure 6. Edge view showing the knife blade (glass slide) positioned above the substrate (silicon wafer) at a given gap height (typically ~200 μm). Gap height in this figure is exaggerated for illustrative purposes only.

contacts the surface of the substrate. Next, (2) visually check the alignment of the blade and make adjustments to the tilt stage until the entire blade contacts the surface. This (1)-(2) process should be iterated until acceptable alignment is achieved. The (tip) angle between the blade and substrate should be ~5^{o} relative to the substrate. Finally, the height between the substrate and blade should be adjusted by the aforementioned micrometer to be ~200 μm (see Figure 6).

Film Preparation. The NCMC Flow Coater is operated through a terminal emulator within Motion Architect, a text-based interface supplied by Parker Automation to directly control their motors. The commands are sent to the motors using a PCI card installed in the computer. Within the terminal emulator, the following parameters should be entered:

> SGV 10	- sets the integral gain for the motor
> SGP 10	- sets the proportional gain for the motor
> DRIVE 1	- turns the drive on
> A5	- sets the acceleration to ‘5’ arbitrary units/s/s
> V40	- sets the velocity to ‘40’ arbitrary units/s
> AD200	- sets the deleceration to ‘200’ arbitrary units/s/s
> D350000	- sets the travel distance to ‘350000’ arbitrary units (~50 mm)

At this point, ~50 μL of solution should be syringed under the knife blade. Capillary forces should wick the solution in and hold it there. NOTE: 50 μL is a good rule of thumb for a 25 mm blade, and should be scaled linearly for larger blades.

> GO	- commands the drive to move
> DRIVE 0	- turns the drive off (wait for the motor to stop moving)

In the above example, the values for A, V, and D are the adjustable parameters. For any given system, it is expected that there will be some initial trial and error to find the right parameters for a desired window of thickness. Included in Table I are some examples of the thickness range one might get as a function of the adjustable parameters. The data in Table I should be used as a guide only.

Table I. Film thickness data for polystyrene (Mw ~ 280k) in toluene as a function of adjustable parameters.

Concentration	A	V	AD	D	Thickness
1%	5	100	200	350,000	20 nm – 40 nm
2%	5	100	200	350,000	40 nm – 80 nm
3%	5	100	200	350,000	80 nm – 160 nm
4%	5	100	200	350,000	140 nm – 240 nm
2%	100	10	200	350,000	70 nm
2%	100	20	200	350,000	115 nm
2%	100	30	200	350,000	150 nm
2%	100	40	200	350,000	225 nm

Measuring Film Thickness. We employ a well-known optical technique (spot interferometry) to create thickness maps of the film created via flow coating. This is a commercial instrument that has been integrated into the NCMC Flow Coater. The interferometer is positioned above the sample area of interest and quickly (< 4 seconds) ascertains the thickness of the area. The spot size for this instrument is ~ 0.5 mm, thus the thickness measured will be averaged over that spot size. The user must specify in the software package the nature of the substrate, the refractive index of the overlying film (some materials are preprogrammed in the software), and estimate of the film thickness (+/- 95%). A background spectrum must be acquired upon start-up of the interferometer, and should be taken on a substrate similar to that which the film of interest is on.

The Filmetrics F20 is also equipped to measure on non-reflective substrates (*i.e.* glass slides) but it requires that the substrate be mounted on the base-plate supplied by Filmetrics, thus eliminating the possibility of mapping the thickness using the current automated x-y stages. A representative spectrum acquired by the Filmetrics F20 is shown in Figure 7. The axes are reflectance vs. wavelength, with the continuous (blue) line being the actual spectrum and the abbreviated (red) line being the fit to the data used to calculate the thickness.

To automate the thickness mapping, we employ a Winbatch program to coordinate movement between each translation stage coupled with the Filmetrics F20 interferometer. The Winbatch code is include for demonstration purposes in the Appendix. The Winbatch program collects the thickness data as a function of x-y position and assembles that information in a simple three-column text file. The spectra files can be saved for further inspection or discarded after acquisition.

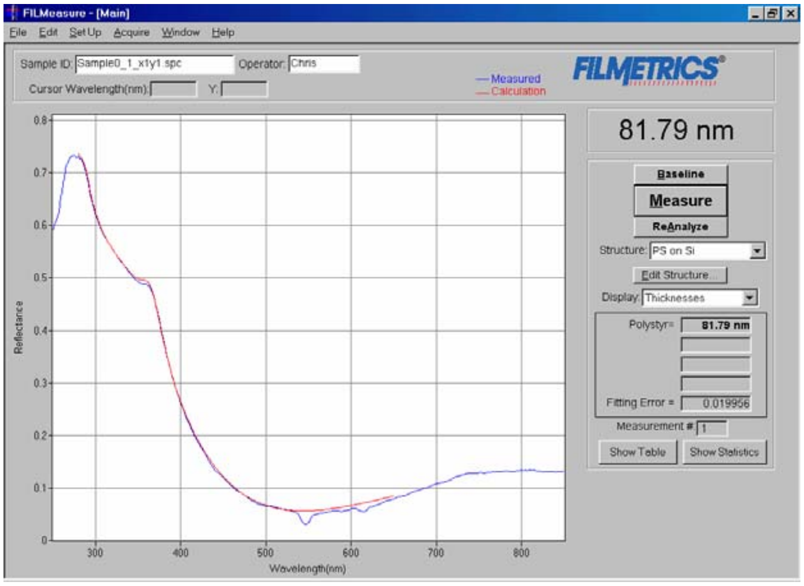

Figure 6. Snapshot of interferometer spectrum and best fit.
The film is comprised of PS on a silicon wafer.

Application Example. A representative example of a thickness gradient is shown in Figure 8. This film was created by flow coating a 4% PS solution in toluene. The adjustable parameters were as follows:

A = 8 V = 100
AD = 200 D = 350,000

A thickness map was created using Filmetrics F20 interferometer. The parameters for mapping thickness were:

12 steps in X, 3 mm per step (33 mm total distance)
8 steps in Y, 3 mm per step (21 mm total distance)

The resulting thickness map can be arranged as either a normal XYZ plot (see Figure 9) or as a contour plot (see Figure 10). The contour plot allows easier visualization of non-linearity in the thickness in both the gradient direction (X) as well as normal to the gradient (Y), while also allowing detection of film defects. In appling this information, one can then program an optical microscope to snap images along specific contour lines to directly follow the effects of film thickness on certain physical properties of the polymer film (phase separation, dewetting, etc.). Conversely, one could snap pictures along the same intervals as were used for measuring the film thickness, and then conduct an off-line ‘morph-ing’ of the data to straighten the contour lines for simpler visualization.

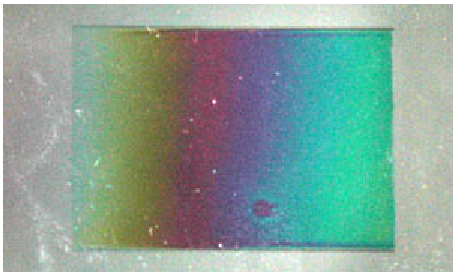

Figure 8. Digital micrograph of a thin film thickness gradient on silicon wafer.

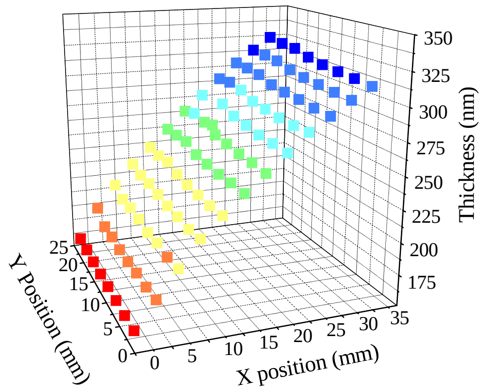

Figure 9. Interferometry data from thickness gradient shown in Figure 7.

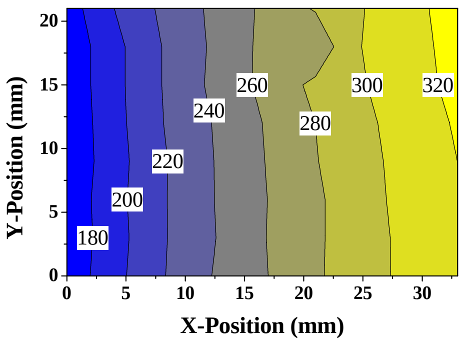

Figure 10. Contour plot of thickness data shown in Figure 9.

Appendix. Computer Automation Software

Given below is an example of a simple WinBatch program created to coordinate the stage motion and Filmetrics data acquisition for mapping out a thickness gradient. The program needed to interface with two different motor control programs (X-axis and Y-axis) as well as the interferometer. The dimensions of the 2-D array to be mapped are gathered via simple dialogue boxes that ask for the user's input. The output is a three-column text file containing x-position, y-position, and thickness. This text file can then be imported into Excel, Origin, SigmaPlot, Igor, or any other database or graphing program.

```
;  Thickness Automation 2D.wbt
;
;  winbatch file to automate the thickness measurements of thin films
;  using the filmetrics UV-visible ellipsometer.  This use a two dimensional
;  motor setup so that the entire film can be scanned automatically.
;  input parameters are   directories, filenames, stepsizes, number of steps.
;  motors are the Parker motor on the flow coater and the Daedel motor in the ;  x direction
;  each filmetrics spectrum is saved in addition to a three column text file
;  containing the x and y positions and the film thickness at that point.
;
;  Based on the 1D program by Carson Meredith
;
;  Written 11/30/00 by A. P. Smith

; Messages to the user and program inputs
Message("FILMeasure Automation","This program automates measurement of thickness using the
FILMetrics F20.")
Message("FILMeasure Automation","Make sure the FILMetrics F20 program is running%@crlf%and the
baseline scans have been acquired.")

:another

directory=AskLine("Filename","What is the directory to save files under?%@crlf%Program assumes
C:\My Documents\ as the beginning.","")

FILE=AskLine("Filename","What is the filename prefix for the Filmetrics spectra files?","")

txtfile = AskLine("Filename","What is the filename for the three column text output?","")

DirMake("C:\My Documents\%directory%")

delx=AskLine("Motor Translation Parameters","Please enter the measurement spacing for x in mm. This
is the bottom motor","")
numx=AskLine("Motor Translation Parameters","Please enter the total number of points for x.","")
xpos = Int(delx*9842.5)

dely=AskLine("Motor Translation Parameters","Please enter the measurement spacing for y in mm. This
is the top motor","")
numy=AskLine("Motor Translation Parameters","Please enter the total number of points for y.","")
ypos = Int(dely*8192)

; INITIALIZE THE COMPUMOTOR APEX 6151, for the y axis
Run("C:\MA6000\EM6000.exe","")
TimeDelay(3)
```

```
SendKeysTo("APEX615N:COM1","SGP10{ENTER}")
SendKeysTo("APEX615N:COM1","SGV10{ENTER}")
SendKeysTo("APEX615N:COM1","A5{ENTER}")
SendKeysTo("APEX615N:COM1","V5{ENTER}")
SendKeysTo("APEX615N:COM1","drive1{ENTER}")
TimeDelay(1)


; initialize the motor velocity, acceleration for the x motor
Run("C:\Program Files\Pc21\VBPC21.exe","")
TimeDelay(3)

SendKeysTo("PC21 Terminal","!c")
SendKeysTo("PC21 Terminal","^{DOWN 9}")
SendKeysTo("PC21 Terminal","!c")
SendKeysTo("PC21 Terminal","A5{ENTER}")
SendKeysTo("PC21 Terminal","V5{ENTER}")

;*****Define Home Position on the grid*****

Zero=Int(0)

;*****HOME POSITION*****

Message("Acquire Background", "Put stage at home position and put sample on stage. Click enter when
finished.")

SendKeysTo("PC21 Terminal","PZ{ENTER}")
SendKeysTo("PC21 Terminal","FSA1{ENTER}")

; Open the text file and enter the initial parameters
Run("C:\Windows\notepad.exe","")
TimeDelay(2)

SendKeysTo("Untitled","x{tab}y{tab}thick{enter}")
SendKeysTo("Untitled","!FS")
SendKeysTo("Save As","C:\My Documents\%directory%\%txtfile%{enter}")
TimeDelay(1)

; Initiate DDE communications with the FILMeasure program
; This is necessary to get out the measured thickness value
channel = DDEInitiate("FILMeasure", "FILMeasureDDE")

; Start Cycling Through thickness measurements
for I = 1 to numx

;       Set up parameters for motor movement
        WinActivate('APEX615N:COM1')
        SendKeysTo("APEX615N:COM1","D-%ypos%{ENTER}")
        back = 0
        delayy = (dely * 0.5) + 1

;       Measure the thickness and save the acquired spectrum
        WinActivate('FILMeasure')
```

```
        SendKeysTo('FILMeasure','!M')
        Timedelay(10)

        SendKeysTo('FILMeasure','!FA')
        SendKeysTo('Save File','C:\My Documents\%directory%\%FILE%_x%I%y1')
        SendKeysTo('Save File','{ENTER}')
        Timedelay(2)

;       acquires the thickness and sends the data to the text file
;       the first line prompts the program to give the value
;       the second line reads the value in.
        getthick = DDEExecute(channel, 'GetThickness(1)')
        thickness = DDERequest(channel, 'DDESourceBox')
        WinActivate('%txtfile%')
        xval = delx * (I-1)
        SendKeysTo('%txtfile%','%xval%{tab}0{tab}%thickness%{enter}')
        TimeDelay(1)


;       now cycle in Y
        for J = 2 to numy

                ;  increment the y motor
                WinActivate('APEX615N:COM1')
                SendKeysTo("APEX615N:COM1","go{ENTER}")
                Timedelay(delayy)
                back = back + ypos

                ;  measure the thickness and save the spectrum
                WinActivate('FILMeasure')
                SendKeysTo('FILMeasure','!M')
                Timedelay(10)

                SendKeysTo('FILMeasure','!FA')
                SendKeysTo('Save File','%FILE%_x%I%y%J%')
                SendKeysTo('Save File','{ENTER}')
                Timedelay(2)

                ;  acquires the thickness and sends the data to the text file
                getthick = DDEExecute(channel, 'GetThickness(1)')
                thickness = DDERequest(channel, 'DDESourceBox')
                WinActivate('%txtfile%')
                yval = dely * (J-1)
                SendKeysTo('%txtfile%','%xval%{tab}%yval%{tab}%thickness%{enter}')
                TimeDelay(1)

        Next

        ;  move the y motor back
        WinActivate('APEX615N:COM1')
        SendKeysTo("APEX615N:COM1","D%back%{ENTER}")
        SendKeysTo("APEX615N:COM1","go{ENTER}")
        Timedelay(delayy*numy/2)

        ;  increment the x motor
```

```
	WinActivate('PC21 Terminal')
	xposition = xpos * (I)
	SendKeysTo("PC21 Terminal","D-%xposition%{ENTER}")
	SendKeysTo("PC21 Terminal", "G{ENTER}")
	Timedelay(2)

	; save the text file
	WinActivate('%txtfile%')
	SendKeysTo('%txtfile%','!FS')
	TimeDelay(1)

Next

; send x motor home
WinActivate('PC21 Terminal')
SendKeysTo("PC21 Terminal","D0{ENTER}")
SendKeysTo("PC21 Terminal","G{ENTER}")
Timedelay(10)

; shut down y motor
WinActivate('APEX615N:COM1')
SendKeysTo("APEX615N:COM1","Drive0{ENTER}")

; Terminate Communications with FILMetrics program
DDETerminate(channel)

; Close Programs
WinActivate('PC21 Terminal')
SendKeysTo('PC21 Terminal','!E')
TimeDelay(1)
;WinActivate('%txtfile%')
;SendKeysTo('%txtfile%','!FX')
;TimeDelay(1)
WinActivate('APEX615N:COM1')
SendKeysTo("APEX615N:COM1","!FXN")
TimeDelay(1)

; Ask if the user wants to do another film
again = AskYesNo('Another Film','Would you like to characterize another film?')
if again == @Yes then Goto another
```